

CLAIMS

1. An organic positive coefficient thermistor comprising: at least
5 two types of polymer matrices, a low molecular weight organic compound, and electrically conductive particles having spike-shaped projections.

2. The organic positive coefficient thermistor according to claim 1,
10 containing electrically conductive particles, wherein the at least two types of polymer matrices are at least one type of thermoplastic polymer matrix and at least one type of heat-curable polymer matrix.

3. The organic positive coefficient thermistor according to claim 2,
15 wherein the heat-curable polymer matrix is either an epoxy resin, unsaturated polyester resin, polyimide, polyurethane, phenolic resin or silicone resin.

[0016] [Means for Solving the Problems] The above-mentioned object is achieved by the present invention as described below.

(1) An organic positive coefficient thermistor comprising: at least
20 two types of polymer matrices, a low molecular weight organic compound, and electrically conductive particles having spike-shaped projections.

(2) The organic positive coefficient thermistor described in (1) above, containing electrically conductive particles, wherein the at
25 least two types of polymer matrices are at least one type of thermoplastic polymer matrix and at least one type of heat-curable

polymer matrix.

(3) The organic positive coefficient thermistor described in (2) above, wherein the heat-curable polymer matrix is either an epoxy resin, unsaturated polyester resin, polyimide, polyurethane, phenolic resin or silicone resin.

[0019] In addition, since a low molecular weight organic compound is contained, and PTC characteristics are demonstrated by which resistance values increased accompany an increase in temperature as a result of dissolving this low molecular weight organic compound, hysteresis of a temperature-resistance curve becomes smaller as compared with the case of using a thermoplastic polymer for the operating substance. In addition, in comparison with the case of adjusting operating temperature using a change in polymer melting point, the operating temperature can be easily adjusted by using low molecular weight organic compounds having different melting points. Moreover, in the present invention, the operating temperature can be made to be 200°C or lower, and more preferably 100°C or lower, by using a low molecular weight organic compound having a melting point of 40 to 200°C and more preferably 40 to 100°C for the operating substance. In addition, differing from the case of using a heat-curable polymer for the operating substance, there is a rapid rise in resistance during operation.

[0020] Moreover, at least two types of polymer matrices are used in the present invention. In the case of a composition consisting only of a low molecular weight organic compound and electrically

conductive particles, the shape of the device cannot be maintained during operation due to the low melt viscosity of the low molecular weight organic compound as previously described. The use of a polymer matrix makes it possible to prevent flow caused by melting of the low molecular weight organic compound during operation, deformation of the device and the like. In addition, if two or more types of polymer matrices, and more specifically, two or more types of thermoplastic polymer matrices having different melting points, or one or more types of thermoplastic polymer matrices and one or more types of heat-curable polymer matrices, are used, characteristics stability improves considerably and low room temperature resistance and large changes in resistance during operation are stably maintained over a long period of time. This effect is particularly remarkable during accelerated high temperature and high humidity testing and intermittent load testing.

[0021] Although a large change in resistance during operation is obtained in the present invention by utilizing volumetric expansion accompanying melting of a low molecular weight organic compound, in the absence of a polymer matrix, the low molecular weight organic compound flows easily due to its low melt viscosity, thereby causing the device to deform considerably even after a single operation. Consequently, thermal deformation is inhibited by dispersing a low molecular weight organic compound in a non-dissolving, non-melting crosslinked polymer matrix having a melting point higher than the low molecular weight organic compound.

[0042] There are no particular limitations on the heat-curable polymer matrix, and epoxy resin, unsaturated polyester resin, polyimide, polyurethane, phenolic resin or silicone resin is used preferably.

5 [0043] Epoxy resins are resins in which an oligomer (having a molecular weight of several hundred to about ten thousand) having a reactive epoxy group on the terminal thereof is cured (crosslinked) with various curing agents, and are classified into glycidyl ether types as typically represented by bisphenol A, glycidyl ester types, glycidyl
10 amine types and alicyclic types. Multifunctional epoxy resins having three or more functional groups can also be used depending on the application. In the present invention, a glycidyl ether type, and particularly bisphenol A, is used preferably. The epoxy equivalent of the epoxy resin used is preferably about 100 to 500. Curing agents
15 are classified into polyaddition types, solvent types and condensation types according to the reaction mechanism. Polyaddition types are such that the curing agent itself is added to an epoxy group or hydroxyl group, examples of which include polyamines, acid anhydrides, polyphenols, polymercaptans and isocyanates. Solvent
20 types catalyze polymerization among epoxy groups, examples of which include tertiary amines and imidazoles. Condensation types induce curing by condensing with a hydroxyl group, examples of which include phenolic resins and melamine resins. In the present invention, a polyaddition type, and particularly a polyamine or acid
25 anhydride, is preferably used for the curing agent of bisphenol A-type epoxy resin. The curing conditions may be suitably determined.

[0044] These types of epoxy resins and curing agents are available commercially, examples of which include Epicoat (resin), Epicure and Epomate (curing agent) manufactured by Yuka-Shell Epoxy Co., Ltd., and Araldite manufactured by Nihon Ciba-Geigy K.K.

[0055] Although the heat-curable resin used can be suitably selected according to the desired performance and application, epoxy resin or unsaturated polyester resin is used preferably. In addition, two or more types may be mutually reacted to form a polymer.

[0128] <Example 5> A heat-curable polymer matrix in the form of bisphenol A epoxy resin (Yuka-Shell Epoxy Co., Ltd., product name: Epicoat 801), a denatured-amine curing agent (Yuka-Shell Epoxy Co., Ltd., product name: Epomate B002), a thermoplastic polymer matrix in the form of low-density polyethylene (Japan Polychem Corp., product name: LC500, MFR: 4.0 g/10 min., melting point: 106°C), a low molecular weight organic compound in the form of paraffin wax (Nippon Seiro Co., Ltd., product name: HNP-10, melting point: 75°C), and electrically conductive particles in the form of filamentous nickel powder (INCO TNC Ltd., product name: Type 255 Nickel Powder) were used. The mean particle diameter of the electrically conductive particles is 2.2 to 2.8 μm , the apparent density is 0.5 to 0.65 g/cm^3 and the specific surface area is 0.68 m^2/g .

[0129] 20 g of bisphenol A epoxy resin, 10 g of denatured amine curing agent, 8 g of low-density polyethylene, 38 g of paraffin wax, 300 g of nickel powder and 30 ml of toluene were mixed for about 10

minutes with a centrifugal disperser. After coating the resulting paint-like mixture on one side of a nickel foil electrode having a thickness of 30 μm , the mixture was sandwiched in between with another nickel foil electrode, placed between brass plates and adjusted to a total thickness of 1 mm with spacers followed by heat-curing for 3 hours at 80°C while pressed together with a hot press. The sheet-like cured product in which the electrodes were hot-pressed was punched out into the shape of a disk having a diameter of 1 cm to obtain an organic positive coefficient thermistor device. A temperature-resistance curve was obtained in the same manner as Example 1 followed by the conducting of accelerated testing and intermittent load testing.

[0130] The initial room temperature resistance of this device was $8.2 \times 10^{-3} \Omega$ ($6.9 \times 10^{-2} \Omega \cdot \text{cm}$), the resistance value increased rapidly in the vicinity of the melting point of the paraffin wax, and the resistance change ratio was 8.2 digits. There were no decreases in resistance (negative temperature coefficient (NTC) phenomena) observed even after increasing the resistance and continuing to heat to 120°C. In addition, the temperature- resistance curve during cooling did not vary greatly from that during heating, and hysteresis was sufficiently small.

[0131] In accelerated testing at 80°C and 80% RH, the room temperature resistance value after 500 hours was $8.8 \times 10^{-3} \Omega$ ($6.9 \times 10^{-2} \Omega \cdot \text{cm}$), demonstrating hardly any change, the resistance change ratio was 7 digits or more, and adequate PTC characteristics were maintained. In addition, there were hardly any NTC phenomena observed after increasing the resistance, and hysteresis was

sufficiently small.

[0132] In intermittent load testing, the room temperature resistance after 500 cycles was $7.8 \times 10^{-3} \Omega$ ($6.1 \times 10^{-2} \Omega \cdot \text{cm}$), demonstrating hardly any change, the resistance change ratio was 7 digits or more, and adequate PTC characteristics were maintained. In addition, there were no NTC phenomena observed whatsoever after increasing the resistance, and hysteresis was sufficiently small.